

Materials on the International Space Station Experiment (MISSE): Optical Analysis of Molecular Contamination on PEC1 Tray 2

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1. Introduction

Materials on the International Space Station Experiment (MISSE) is a program that allows researchers to study the effects of the harsh space environment on a wide variety of materials.¹ The MISSE-1 and -2 payloads consisted of material samples that were in Passive Experiment Containers (PECs) and flown to the International Space Station in August 2001 as a part of the STS-105 mission. The PECs were deployed in two different locations on the outside of the ISS for just over four years and were returned to Earth as a part of STS-114. Each PEC was intended to have a “ram” tray and a “wake” tray. The ram tray would be exposed to UV and the atomic oxygen ram; and the wake tray would only be exposed to UV. PEC 1 Tray 2 was supposed to be on the wake side; however, over the extended mission, the ISS flew in a variety of orientations, and these samples were exposed to 1.1×10^{20} atoms/cm² fluence as measured by polymer erosion.² The UV dose was modeled to be at least 5000 Equivalent Solar Hours (ESH). The location of MISSE1 PEC can be seen in Figures 1 and 2.

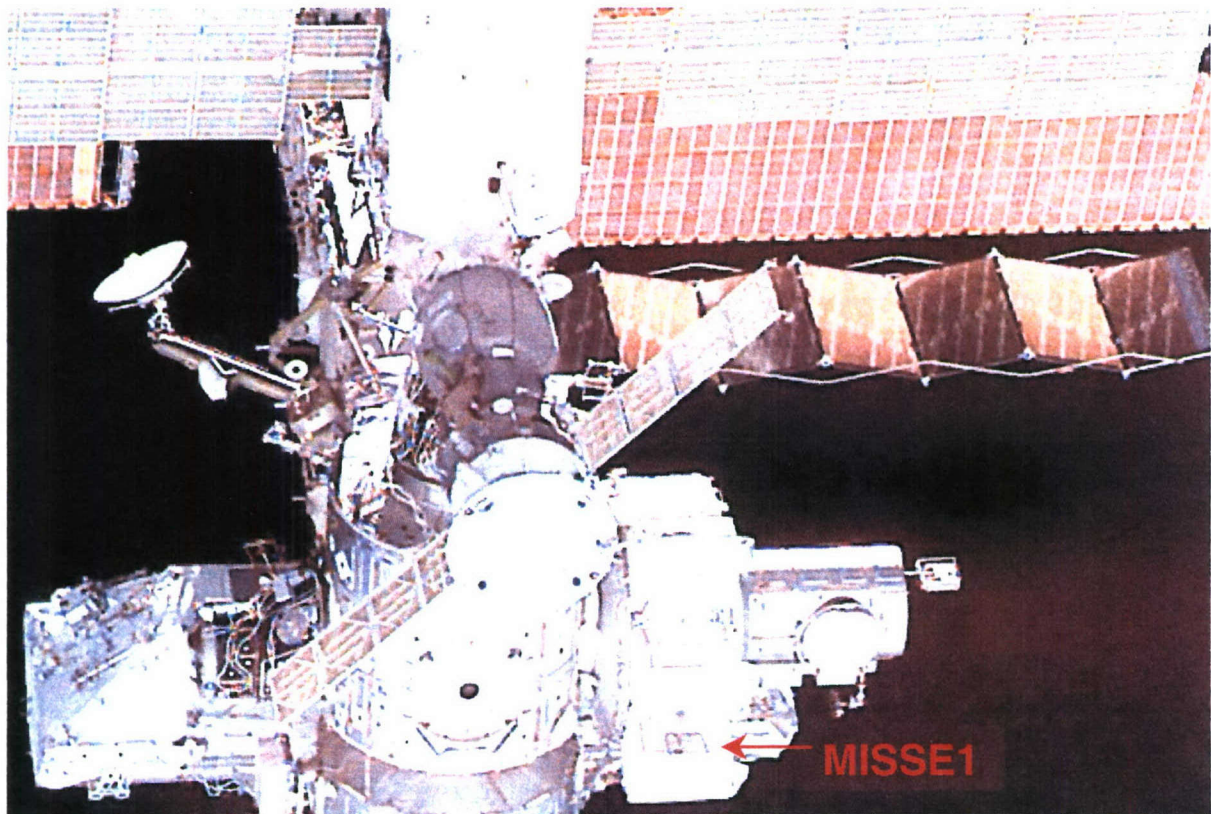


Figure 1. MISSE 1 PEC 1 Tray 2 facing Soyuz. (Courtesy NASA)

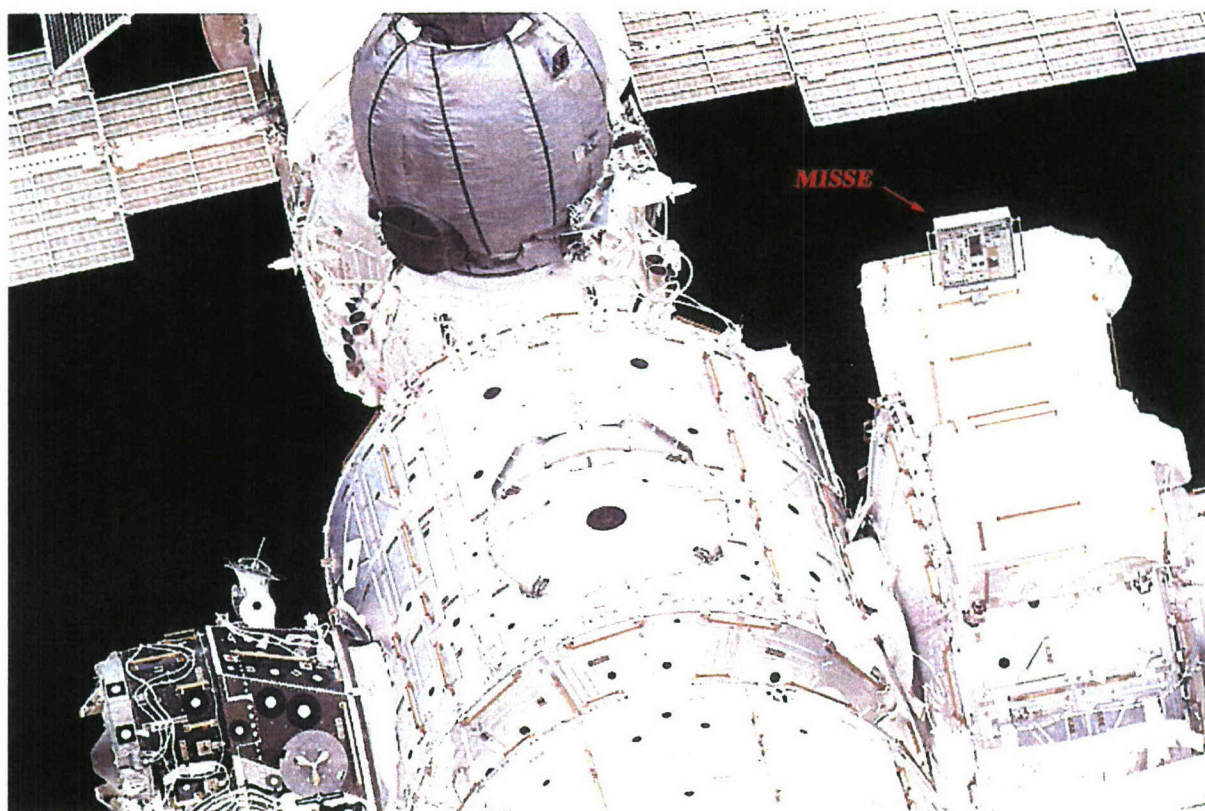


Figure 2. MISSE 1 PEC1 Tray 2 facing away from Soyuz. (Courtesy NASA)

Among the samples mounted in PEC 1 Tray 2 were several bare silicon wafers. Three were exposed to space, and two more were positioned under other samples and were not directly exposed. The unexposed samples served as our control samples. These five silicon wafers were characterized by ellipsometry, reflectometry, and scatterometry, and the results are presented here.

2. Ellipsometry and Reflectometry

Ellipsometric parameters were measured on a Woollam Variable Angle Spectroscopic Ellipsometer running WVASE software. Data was collected in “Isotropic+Depolarization” mode. Polarized reflectance measurements were made at 8° and 40° angles of incidence on a Lambda 950 spectrophotometer with a Universal Reflectance Accessory. Data from 300 nm to 1000 nm was used in the fit optimization routine. Measured values for psi, delta, and reflection are presented in Figures 3 through 7. The samples were optically modeled as three materials—bulk silicon, a thin native oxide, and an unknown material—with Cauchy dispersion (see Eq. 1).

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (1)$$

The Cauchy formula

The index files for silicon and native oxide (silica) were provided with the WVASE software, and they were attributed to Jellison and Palik. Models of the control samples were obtained by optimizing the native oxide thickness. Models of the exposed samples were obtained assuming a fixed native oxide thickness of 22.9 Å, as determined by the fit on the control samples, and then optimizing the fit by adjusting the thickness, A, B, and C parameters of the Cauchy layer. The C term was found to be insignificant and therefore was set to zero. The initial assumption was that there was no absorption in the Cauchy layer. Subsequent modeling showed that adding an exponential absorption with two fitting parameters only slightly reduced the overall Mean Squared Error (MSE.) However, the error between the modeled and measured reflectance measurements grew larger. From this information, we concluded that if there is absorption, it is not significant in a coating of this thickness. The dispersion curves for the three exposed samples are given in Figure 9. Note that the derived index curves straddle Palik’s widely accepted curve for silica. Averaging the Cauchy layer thickness on the three exposed samples gives a thickness of 423.6 Å

It is not surprising that silica could be formed on silicon in the presence of atomic oxygen. Certainly, given enough time, a native oxide is always formed on bare silicon in air at room temperature. The growth of that layer tends to terminate at about 20 Å. Exposure to hyperthermal atomic oxygen should enhance that growth rate, and, indeed, that is the case. Silicon wafers exposed to hyperthermal oxygen from a pulsed laser detonation source³ showed enhanced oxidation, but only 45 Å of SiO₂ could be grown at room temperature when exposed to 10¹⁹ oxygen/cm² with an average energy of 5.1 eV. Higher temperatures and longer exposures didn’t significantly increase the thickness. Only 50 Å of silica could be grown on silicon at 493K when exposed to 8 x 10¹⁹ oxygen/cm².⁴ Thus, given an average thickness of 424 Å, it is likely that most of the layer is from an extrinsic source. Certainly, silica has been seen on external spacecraft surfaces before. Zweiner et al. found silica on the Russian space station MIR and hypothesized that the source was silicone that had outgassed, condensed, and been converted by UV light and atomic oxygen.⁵

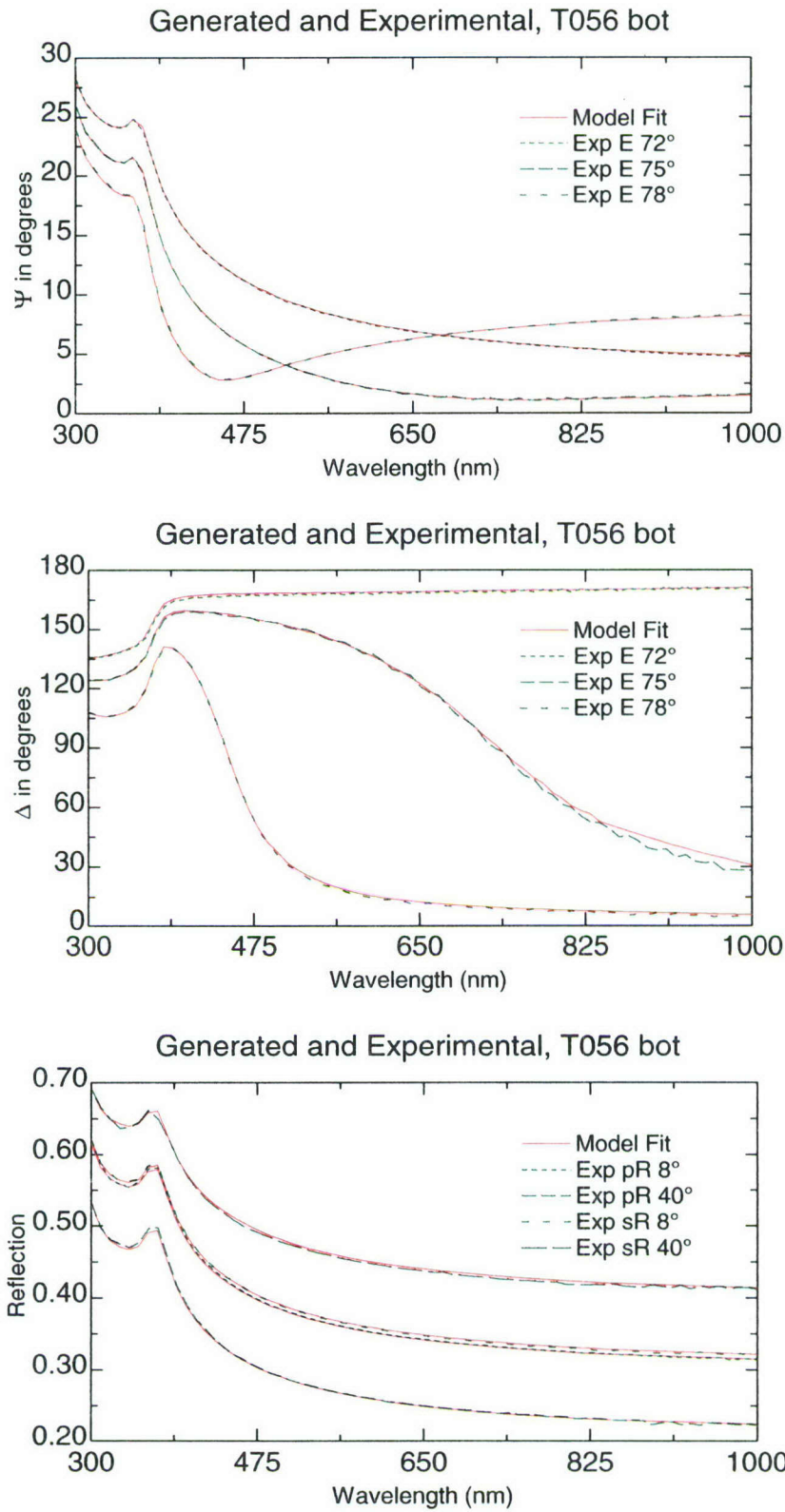


Figure 3. Psi, Del, Reflection data and fits for T056 bot. Native oxide = 22.9 Å

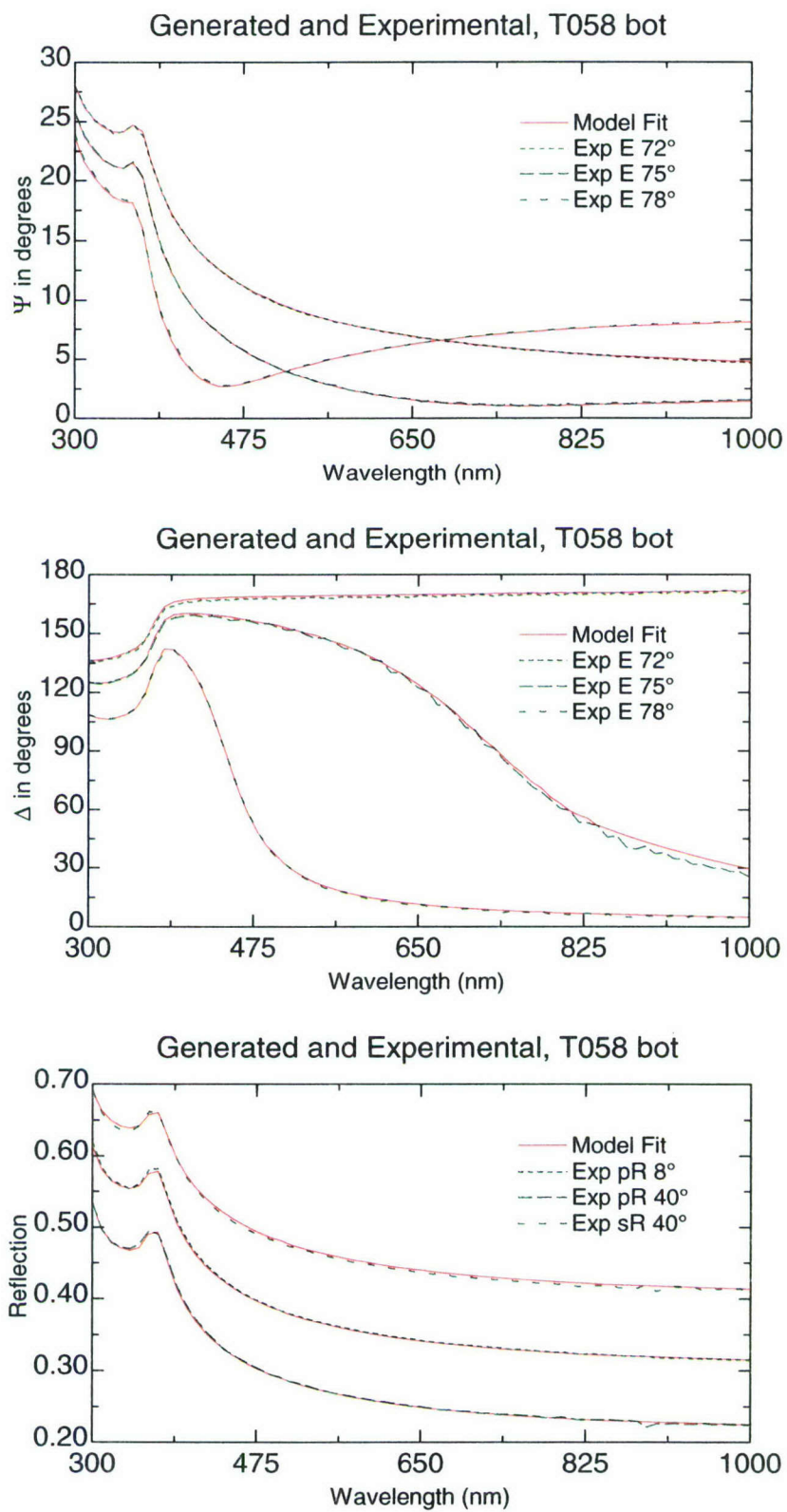


Figure 4. Psi, Del, Reflection data and fits for T058 bot. Native oxide = 21.8 Å

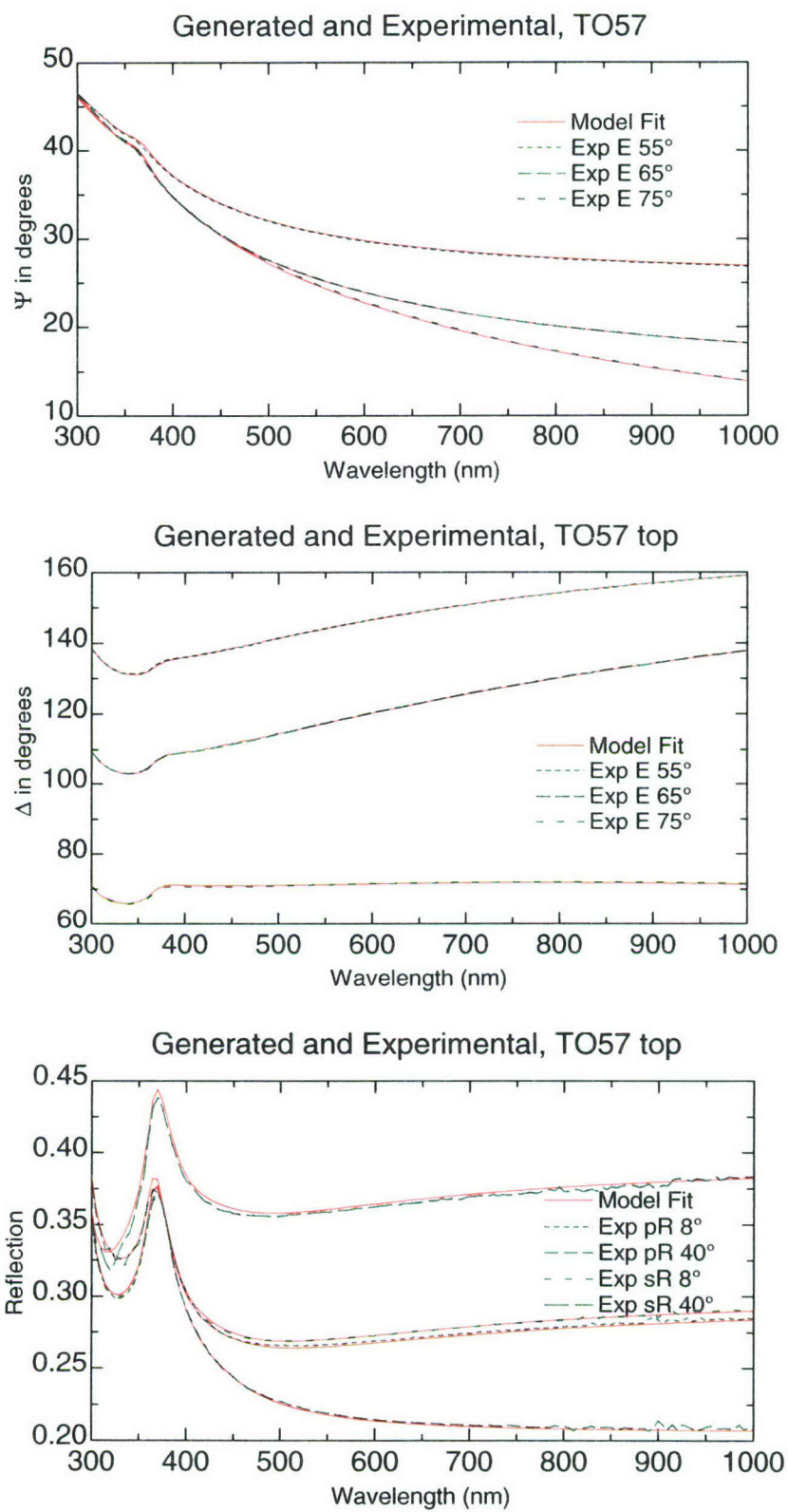


Figure 5. Psi, Del, Reflection data and fits for TO57 top. Cauchy Layer = 419 Å

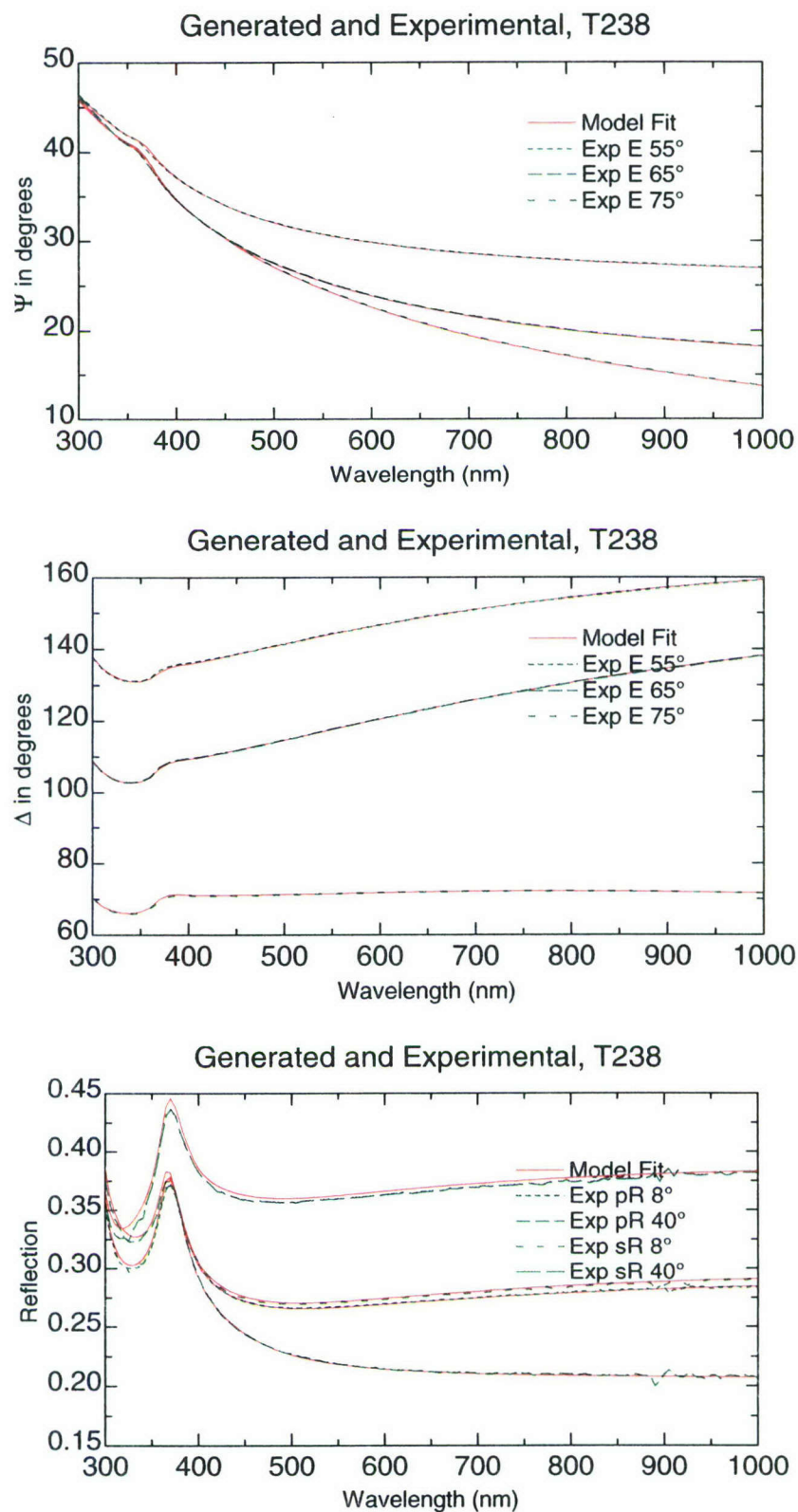


Figure 6. Psi, Del, Reflection data and fits for T238 bot. Cauchy Layer = 417Å

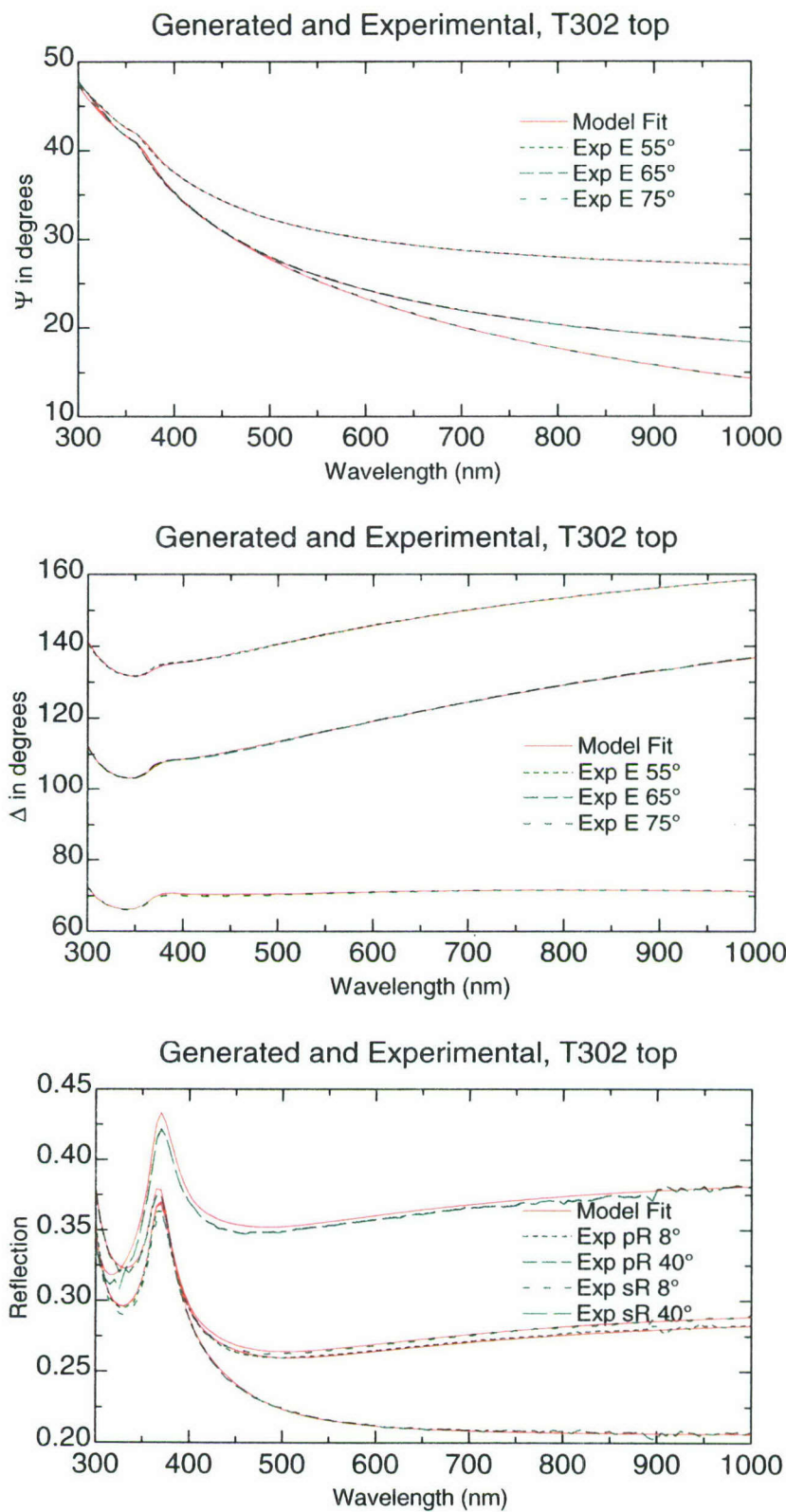


Figure 7. Psi, Del, Reflection data and fits for T302 Cauchy Layer = 434Å

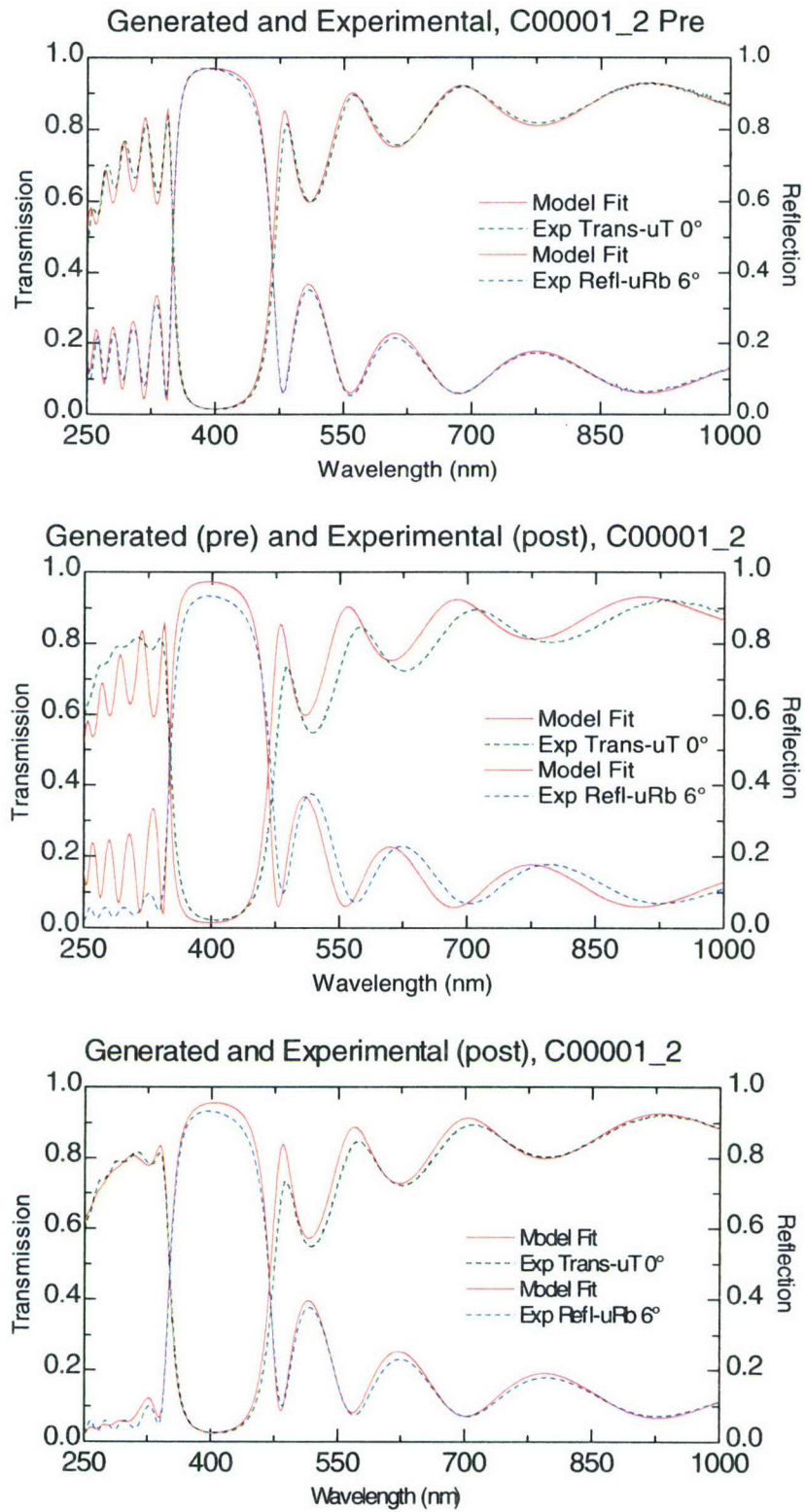


Figure 8. Transmission and Reflection of a dielectric stack. The fit is improved with an additional 424 Å of the Cauchy layer with $A=1.455$, $B=0.0028$, and $C=0$. *See text.*

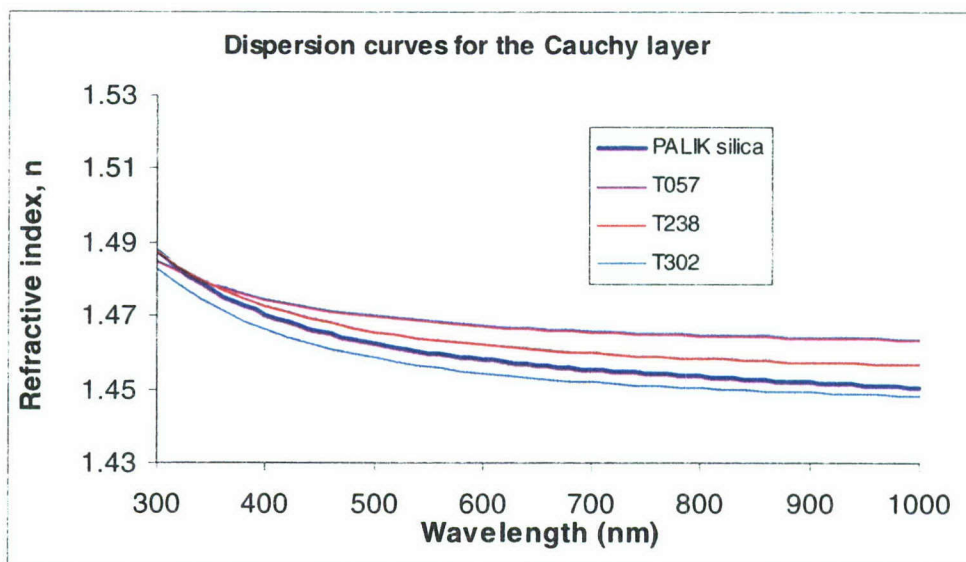


Figure 9. Dispersion curves for the Cauchy layer (with Palik values.).

Further evidence of an extrinsic source can be found in Figure 8, which shows the reflectance and transmittance of a 13-layer zirconia/silica dielectric stack that was also flown on TRAY 2, EOIM 11 of MISSE 1. Zirconia is the top (exposed) layer. The first graph shows how the generated model fits the transmittance and reflectance curves for the sample before exposure. The second figure retains the generated curves and adds the post-exposure-measured curves to show that the spectra changed significantly. The final curves show the post-flight spectra with an additional 424 Å Cauchy layer ($A = 1.455$, $B = 0.0028$, $C = 0$) that is consistent with the layers found in Table 1. The fit is not perfect, but quite convincing. The mean-squared error drops from 0.97 to 0.33 with the additional layer. Growth of a silica layer on a zirconia layer could only come from an extrinsic source.

Table 1. Optical Modeling of MISSE 1 Silicon Samples

	CONTROL		EXPOSED		
Serial Number	T056 bot	T058 bot	T057 top	T238	T302
Native Oxide	22.9 Å	21.8 Å	22.9 Å	22.9 Å	22.9 Å
MSE=			0.512	0.656	0.7577
Cauchy Thickness (Å)			419.5±0.42	417.19±0.38	434.22±0.41
Cauchy, A			1.461±0.0011	1.4538±0.00106	1.4488±0.00108
Cauchy, B (um ⁻²)			0.00208±0.00014	0.00304±0.00011	0.00342±0.000107

3. Scatterometry

Scatter from these samples was measured with a Schmitt Measurement Systems MicroScan hand-held fixed-angle scatterometer.⁶ The results are presented below. With no sample, the noise equivalent BRDF is 1.2×10^{-6} and 4.3×10^{-7} reciprocal-steradians for $\beta - \beta_0 = 0.4$ and 1.2 , respectively. A fresh, clean silicon wafer was measured at 6.4×10^{-6} and 3×10^{-6} , at the same angles. The “control” samples were mounted under other samples in the MISSE1 tray. It is not surprising that they show slightly increased scatter as a result of the complicated process of integration, launch, deployment, and recovery. The samples that were exposed to the space environment, with the aforementioned deposited layer, had average BRDF values of about 1×10^{-4} at $(\beta - \beta_0 = 0.4)$ and about 4.5×10^{-5} at $(\beta - \beta_0 = 1.2)$.

Table 2. BRDF of Silicon Flown on MISSE 1

MISSE1Code	Sample Name	BRDF	
		$(\beta - \beta_0 = 0.4)$	$(\beta - \beta_0 = 1.2)$
	None (NEBRDF)	1.2×10^{-6}	4.3×10^{-7}
	Uncoated Fresh Si	6.4×10^{-6}	3.0×10^{-6}
-2-E12-34	T056 Ctrl	1.7×10^{-5}	2.0×10^{-5}
-2-E12-35	T058 Ctrl	1.2×10^{-5}	5.0×10^{-6}
-2-E12-26	T302 Exp	9.2×10^{-5}	4.0×10^{-5}
-2-E12-35	T057 Exp	1.1×10^{-4}	5.1×10^{-5}
-2-E12-36	T238 Exp	9.6×10^{-5}	4.3×10^{-5}

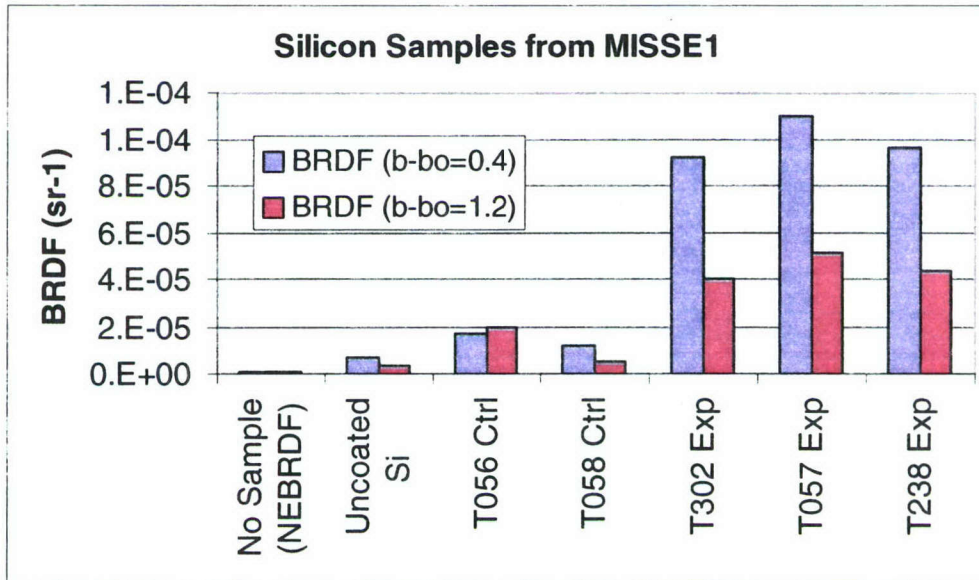


Figure 10. BRDF of silicon flown on MISSE.

4. Conclusions

Silicon wafers flown on the MISSE 1 experiment that were exposed to the space environment and then returned to Earth were found to have an externally deposited layer with an index of refraction consistent with silicon dioxide having a thickness of about 400 Å. The properties of this layer were measured via ellipsometry and reflectometry. These samples also exhibited substantially increased scatter over silicon wafers that were flown on MISSE 1, but which were not exposed to the space environment. We suspect that the primary source for this deposited layer is the deposition of silicone contaminants that were simultaneously or subsequently converted to silicon dioxide via exposure to the atomic oxygen environment found in the ISS orbit.

References

1. More information can be found at <http://misseone.larc.nasa.gov/>. Links to information on earlier materials experiments (Long Duration Exposure Facility, LDEF; and Mir Environmental Effects Payload, MEEP) can be found at <http://setas-www.larc.nasa.gov/index.html>.
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